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Synthesis of *N*-Sulfonyl Aziridines Through Regioselective Opening of Epoxides Under Solid-Liquid PTC Conditions

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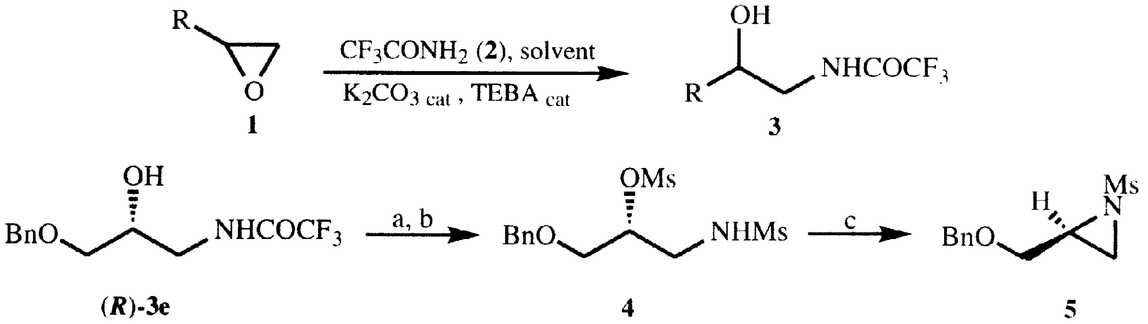
Abstract: The ring opening of epoxides **1** with 4-toluenesulfonamide (**6**) under solid-liquid phase transfer catalysis (SL-PTC) conditions afforded regioselectively β-sulfonamidoalcohols **7** in high yields. These were further converted into *N*-sulfonylaziridines **9** after activation of the hydroxy leaving group followed by ring closing in the presence of potassium carbonate. © 1999 Elsevier Science Ltd. All rights reserved.

The importance of aziridines as versatile synthetic intermediates,[1] chiral auxiliaries and ligands for stereoselective synthesis[2] is well known. They are frequently prepared through the three steps ring closure of β-amino alcohols derived from natural amino acids even though this method is limited by the availability of the amino acids. Alternative procedures are alkene[3] and imine aziridination[4] along with the nitrogen nucleophilic ring opening of epoxides.[5] The latter strategy appears particularly attractive and more flexible due to recent advances in the development of enantioselective methods for the synthesis of epoxides.[6]

In a previous paper we have reported on the synthesis of β-hydroxytrifluoroacetamides **3** by ring opening of epoxides **1** with trifluoroacetamide (**2**) under solid-liquid phase transfer catalysis (SL-PTC) conditions.[7] Due to the easy removal of the trifluoroacetamide group by mild alkaline hydrolysis, hydroxyamides **3** can be considered synthetic equivalents of the β-amino alcohol moiety,[7] thus representing valuable intermediates for the synthesis of aziridines. For example (2*R*)-(-)-1-*N*-(trifluoroacetyl)-3-(phenylmethoxy)propan-2-ol (**3e**), obtained from (*S*)-**1e**, has been converted into aziridine **5** in 87% overall yield through the procedure depicted in Scheme 1.



a) NaOH 3%/THF 0°C, 1 h; 98%. b) MsCl, Et_3N, CH_2Cl_2; 92%. c) K_2CO_3, $TEBA_{cat}$, CH_3CN 1 h, 45 °C; 96%.

Scheme 1

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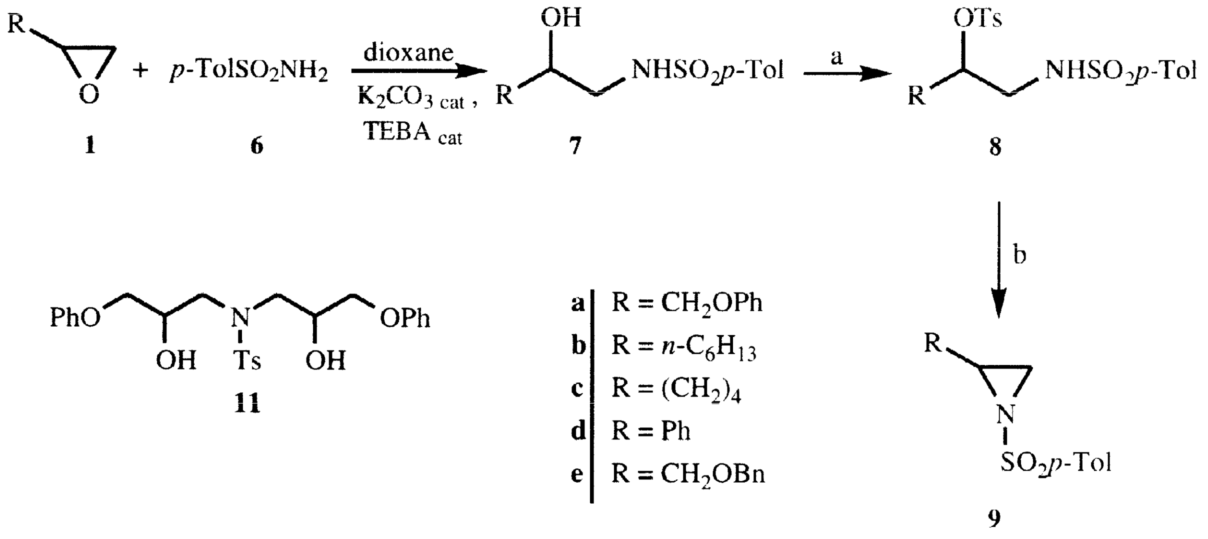
In order to optimise the conversion of epoxides into aziridines, 4-toluenesulfonamide (**6**) was investigated as a tool to deliver and protect the aziridine nitrogen. Herein we wish to report that excellent yields of *N*-tosylamino alcohols **7** were obtained by ring opening of **1** with **6** under SL-PTC conditions. Moreover the selective *O*-tosylation of **7** followed by ring closing of the resulting **8** produced the aziridines **9** in high overall yields (Scheme 2).



a) TsCl, Py, CH_2Cl_2. b) K_2CO_3, CH_3CN.

Scheme 2

RESULTS AND DISCUSSION

The ring opening was performed by stirring at 90 °C a heterogeneous mixture of the epoxide **1** (1 mol), triethylbenzylammonium chloride (TEBA) (**10**) (0.1 mol), anhydrous K_2CO_3 (0.1 mol), 4-toluenesulfonamide (**6**) (2 mol) and dioxane as solvent. Under these reactions conditions β-amido alcohols **7a-e** were isolated in 75-93% yield after 2.5-12 h (Table 1).[8] As expected, the reaction takes place in a complete regioselective fashion affording β-amido alcohols **7** deriving from the nucleophilic attack to the less substituted carbon atom of the oxirane ring. As a consequence of the observed regiochemistry non racemic epoxides generate enantiopure β-amido alcohols, as confirmed in the case of (2*S*)-(+)-[(Phenylmethoxy)methyl]oxirane (**1e**). The enantiomeric purity of (*R*)-**7e** was determined by 300 MHz ^1H NMR analysis of Mosher derivatives. In fact the Mosher's ester prepared from (*R*)-**7e** and (*R*)-Mosher acid chloride[9] showed a single signal for the methoxy group at 3.507 ppm, whereas the diastereoisomeric esters obtained from racemic **7e** showed two separated singlets at 3.507 and 3.488 ppm.

The presence of the PTC agent **10** is essential in order to obtain high yields of β-sulfonamido alcohols in short reaction times. In fact the catalysed ring opening of [(phenoxy)methyl]oxirane (**1a**) afforded 75% of **7a** in 2.5 h, whereas 11 h were necessary to generate 54% of **7a** in the absence of TEBA. Sodium and cesium carbonate were found to be less selective bases for the mono-*N*-alkylation of **6**. In fact **7a** was generated in 45-60% yield together with 43-34% of the dialkylated byproduct **11**.[10]

Table 1. *β*-Amido Alcohols **7** Prepared by Opening of Epoxides **1**

epoxide **1**	t (h)	yield (%)	β-sulfonamido alcohol
(±)-**1a**	2.5	75	(±)-**7a**
	11	54[a]	
(±)-**1b**	6	91	(±)-**7b**
(±)-**1c**	12	93	(±)-**7c**
(±)-**1d**	6	93	(±)-**7d**
(*S*)-**1e**	2	85	(*R*)-**7e**

[a] Without TEBA.

The selective *O*-tosylation of **7a-e**, required for the activation of the hydroxy leaving group, was carried out with tosyl chloride and pyridine in dichloromethane affording *N,O*-ditosyl derivatives **8a-e** in 80-92% yield. In the case of 1-*N*-tosyl-2-phenyl-1-ethanol (**7d**) only the corresponding *N*-(2-chloro-2-phenylethyl)-4-(methylphenyl)sulfonamide (**12**) was isolated in low yield.[11]

N-Sulfonyl aziridines **9a-e** were produced by stirring at 45°C an acetonitrile solution of *N,O*-ditosyl derivatives **8a-e** in the presence of an excess of anhydrous potassium carbonate. It is worth noting that they can be isolated as pure compounds in quantitative yields after an aqueous work-up. The ring closing to aziridines takes place even at room temperature, although in longer reaction times. In this case faster reactions can be obtained in the presence of catalytic amounts of TEBA (Table 2). For example **8c** afforded 96% of *N*-(4-methylphenylsulfonyl)-7-azabicyclo[4.1.0]heptane (**9c**) after 40 min at 45°C, whereas 60 and 120 minutes were necessary at 20°C in the presence or without TEBA, respectively.

Table 2. *N,O*-Ditosyl derivatives **8** and Aziridines **9** Prepared

	ditosyl **8** (%)	t (h)	aziridine **9** (%)	t (min)
a	92	5	96	40
b	84	13	97	60
c	82	24	96	40
c			97	60[a]
c			98	120[b]
d	-	-	76[c]	-
e	83	24	97	40

[a] At 20°C with TEBA (0.1 equiv). [b] At 20°C. [c] Obtained through ring closure of **7d** under Mitsunobu conditions.[13]

It is well known that the *N*-tosyl function is a quite robust one and can tolerate a wide variety of harsh reaction conditions, moreover the *N*-tosyl moiety is well suited to activate aziridines to nucleophilic ring opening. However in many cases a more easily removable group is preferred due to the presence of sensitive functionalities unable to survive normal deprotection conditions. Due to recent advances in the cleavage of nitroaryl sulfonamides[14] and being aware of the stronger activating power to nucleophilic ring opening of the nitroarylsulfonyl moiety,[13] 2-nitrophenylsulfonamide can be used instead of 4-toluenesulfonamide (**6**) as shown in experimental.

In conclusion we showed that β-sulfonamido alcohols **7** can be efficiently generated by regioselective ring opening of epoxides **1** under SL-PTC conditions, thus allowing the synthesis of polyfunctionalised building blocks bearing a stereocenter of known configuration. A chemically robust or easily removable *N*-sulfonyl moiety can be produced as convenient by the opportune choice of the arylsulfonamide **6**. β-Sulfonamido alcohols **7** are converted to aziridines in good overall yields. In the case of sensitive substrates the ring closure to aziridines can be carried out at room temperature, if necessary in the presence of a PTC agent in order to speed up the reaction.

Acknowledgements

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EXPERIMENTAL

Epoxides **1a-e** are commercially available. K_2CO_3 was dried by heating at 140°C in vacuum (0.05 mmHg) for 6 h. ^1H NMR spectra were recorded in $CDCl_3$ at 300 MHz using TMS as external standard. The coupling costants are in Hz. IR spectra were recorded on a FT-IR 1725 Perkin Elmer spectrometer and frequency values are in cm^{-1}. Optical rotations were measured with a Perkin Elmer 241 instrument. Melting points are corrected. Analytical TLC was performed using Merck precoated silica gel F_{254} plates.

Synthesis of (2*S*)-*N*-Methanesulfonyl-2-[(phenylmethoxy)methyl]aziridine (5).

(2*R*)-(-)-1-*N*-(Trifluoroacetyl)-3-(phenylmethoxy)propan-2-ol (**3e**) (3 mmol, 832 mg) was dissolved in THF (3 ml) and NaOH 3% (6 mmol, 7.8 ml) was added. After stirring for 1h at 0 °C the solvent was evaporated and the residue extracted with Et_2O. The organic solution was dried ($MgSO_4$), filtered and evaporated to give 533 mg (98% yield) of (2*R*)-1-amino-3-benzyloxy-2-propanol, mp 61-62 °C, $[\alpha]_D^{20} = -4.64$ (c = 0.01, CH_2Cl_2). ^1H NMR ($CDCl_3$), δ, 1.77 (bs, 3H), 2.72 (dd, 1H, *J* = 7.1 and 12.9), 2.83 (dd, 1H, *J* = 4.1 and 12.9), 3.44 (dd, 1H, *J* = 6.4 and 9.6), 3.51 (dd, 1H, *J* = 4.1 and 9.6), 3.75 (m, 1H), 4.54 (s, 2H), 7.25-7.37 (m, 5H).

(2*R*)-1-Amino-3-benzyloxy-2-propanol was dissolved in 10 ml of CH_2Cl_2 and Et_3N (5.90 mmol, 597 mg) was added. A solution of freshly distilled MsCl (6 mmol, 687 mg) in CH_2Cl_2 was added dropwise at 0 °C and the resulting mixture stirred at the same temperature for 2 h. The crude was subjected to flash column chromatography [AcOEt-petroleum ether (PE) 2:3] affording 912 mg (92% yield) of (2*R*)-1-(methanesulfonyl)amino-2-(methanesulfonyl)oxy-3-(phenylmethoxy)propane (**4**); mp 101-102 °C $[\alpha]_D^{20} = -3.11$ (c = 0.01, CH_2Cl_2). ^1H NMR ($CDCl_3$), δ, 2.98 (s, 3H), 3.06 (s, 3H), 3.37-3.46 (m, 2H), 3.68 (dd, 1H, *J* = 4.4 and 10.9), 3.74 (dd, 1H, *J* = 5.8 and 10.9), 4.55 (dd, 2H, *J* = 11.8 and 14.2), 4.72 (bs, 1H), 4.85 (m, 1H), 7.27-7.39 (m, 5H). ν_{max} (Nujol) 3372 (NH), 1344 (SO_2O), 1323 (SO_2N), 1171 (SO_2O), 1154 (SO_2N). *Anal. Calcd.* for $C_{12}H_{19}NO_6S_2$: C, 42.72; H, 5.68; N, 4.15. *Found*: C, 42.97; H, 5.91; N, 4.01.

(2*R*)-1-(Methanesulfonyl)amino-2-(methanesulfonyl)oxy-3-(phenylmethoxy)propane (**4**) was dissolved in CH_3CN, treated with K_2CO_3 (10.8 mmol, 1.49 g) and TEBA (0.27 mmol, 62 mg) and stirred at 80 °C for 3 h.

After cooling to room temperature 2 ml of H_2O were added and the crude extracted with Et_2O. The organic solution was dried ($MgSO_4$), filtered and evaporated to give 627 mg (96% yield) of the title compound, $[\alpha]_D^{20}$ = +59.1 (c = 0.01, CH_2Cl_2). ^1H NMR ($CDCl_3$), δ, 2.24 (d, 1H, *J* = 4.6), 2.65 (d, 1H, *J* = 7.2), 2.97 (m, 1H), 3.08 (s, 3H), 3.43 (dd, 1H, *J* = 6.7 and 10.9), 3.71 (dd, 1H, *J* = 3.7 and 10.9), 4.58 (s, 2H), 7.28-7.38 (m, 5H). ν_{max} (Nujol) 1317 (SO_2N), 1153 (SO_2N). *Anal. Calcd.* for $C_{11}H_{15}NO_3S$: C, 54.76; H, 6.27; N, 5.81. *Found*: C, 54.90; H, 6.39; N, 5.92.

General Method for the Preparation of β-Amido Alcohols 7a-e.

A mixture of the epoxide **1** (1 mmol), K_2CO_3 (0.1 mmol, 14 mg), TEBA **10** (0.1 mmol, 23 mg), 4-toluenesulfonamide **6** (2 mmol, 342 mg) and dioxane (0.25 ml) was stirred at 90 °C until the starting material was no longer detectable (TLC analysis). After cooling, the crude was diluted with CH_2Cl_2, filtered on celite and the solvent evaporated under reduced pressure. The residue was purified by MPLC or flash column chromatography on silica gel (230-400 mesh). Starting epoxide, reaction time, chromatographic eluant, yield and physical, spectroscopic and analytical data of **7a-e** are as follows.

1-*N*-(4-methylphenylsulfonyl)amino-3-(phenoxy)propan-2-ol (7a). [(Phenoxy)methyl] oxirane (**1a**); 2.5 h; Et_2O-PE 3:1. **7a**, 75%; mp 63 °C (lit.,[15] 64-66 °C); ^1H NMR ($CDCl_3$), δ, 2.43 (s, 3H), 2.64 (d, 1H, *J* = 4.6), 3.05-3.13 (m, 1H), 3.25 (ddd, 1H, *J* = 3.9, 7.0 and 13.2), 3.91-3.96 (m, 2H), 4.07-4.11 (m, 1H), 6.85 (d, 2H, *J* = 8.1), 6.97 (t, 1H, *J* = 7.4), 7.25-7.32 (m, 4H), 7.75 (d, 2H, *J* = 8.3).

1-*N*-(4-methylphenylsulfonyl)aminooctan-2-ol (7b). 1,2-Epoxyoctane (**1b**); 6 h; Et_2O-PE 3:2. **7b**, 91%; mp 40-41 °C; ^1H NMR ($CDCl_3$), δ, 0.86 (t, 3H, *J* = 6.6), 1.22-147 (m, 10H), 1.91 (d, 1H, *J* = 3.8), 2.42 (s, 3H), 2.77 (ddd, 1H, *J* = 5.1, 8.1 and 12.9), 3.08 (ddd, 1H, *J* = 3.1, 7.5 and 12.9), 3.64-3.71 (m, 1H), 4.91 (t, 1H, *J* = 6.1), 7.31 (d, 2H, *J* = 8.1), 7.74 (d, 2H, *J* = 8.2). ν_{max} (Nujol) 3502 (OH), 3272 (NH), 1318 (SO_2N), 1159 (SO_2N). *Anal. Calcd.* for $C_{15}H_{25}NO_3S$: C, 60.17; H, 8.42; N, 4.68. *Found*: C, 60.34; H, 8.62; N, 4.40.

***trans*-2-*N*-(4-methylphenylsulfonyl)aminocyclohexanol (7c).** Epoxycyclohexane (**1c**); 12 h; Et_2O-PE 7:3. **7c**, 93%; mp 131-132 °C (lit.,[16] 129-130 °C); ^1H NMR ($CDCl_3$), δ, 1.06-1.24 (m, 4H), 1.59-1.78 (m, 4H), 1.98 (bs, 1H), 2.43 (s, 3H), 2.79-2.86 (m, 1H), 3.27 (dt, 1H, *J* = 4.6 and 9.7), 4.59 (d, 1H, *J* = 6.7), 7.31 (d, 2H, *J* = 8.2), 7.77 (d, 2H, *J* = 8.2).

1-*N*-(4-methylphenylsulfonyl)amino-2-phenyl-1-ethanol (7d). Phenyloxirane (**1d**); 6 h; Et_2O-PE 1:1. **7d**, 93%; mp 105-106 °C (lit.,[17] 107-108 °C); ^1H NMR ($CDCl_3$), δ, 2.31 (d, 1H, *J* = 3.5), 2.42 (s, 3H), 3.01 (dd, 1H, *J* = 4.6 and 8.5), 3.05 (dd, 1H, *J* = 5.6 and 8.5), 4.79 (dd, 1H, *J* = 3.6 and 8.6), 5.01 (m, 1H), 7.23-7.34 (m, 7H), 7.72 (d, 2H, *J* = 8.3).

(2*R*)-1-*N*-(4-methylphenylsulfonyl)amino-3-(phenylmethoxy)propan-2-ol (*R*)-7e. (2*S*)-(+)-[(Phenylmethoxy)methyl]oxirane (*S*)-**1e**; 2 h; Et_2O-PE 2:1. (*R*)-**7e**, 85%; mp 74.7-75 °C; $[\alpha]_D^{20}$ = -10.93 (c = 0.84, CH_2Cl_2). ^1H NMR ($CDCl_3$), δ, 1.60 (bs, 1H), 2.42 (s, 3H), 2.93 (ddd, 1H, *J* = 6.1, 6.6 and 12.9), 3.11 (ddd, 1H, *J* = 4.0, 6.1 and 12.9), 3.43 (dd, 1H, *J* = 6.3 and 9.6), 3.49 (dd, 1H, *J* = 4.1 and 9.6), 3.84-3.91 (m, 1H), 4.50 (s, 2H), 4.85 (t, 1H, *J* = 5.9), 7.25-7.32 (m, 7H), 7.72 (d, 2H, *J* = 8.3). ν_{max} (Nujol) 3400 (OH), 3277 (NH), 1331 (SO_2N), 1161 (SO_2N). *Anal. Calcd.* for $C_{17}H_{21}NO_4S$: C, 60.87; H, 6.31; N, 4.18. *Found*: C, 61.17; H, 6.59; N, 4.00.

1-*N*-(2-Nitrophenylsulfonyl)amino-3-(phenoxy)propan-2-ol (13). The title compound was prepared by using 2-nitrophenylsulfonamide (1.1 equiv) instead of **6**. [(Phenoxy)methyl] oxirane (**1a**); 6 h; Et_2O-PE 2:1. **13**, 89%; oil; ^1H NMR ($CDCl_3$), δ, 2.50 (bs, 1H), 3.21-3.30 (m, 1H), 3.41 (ddd, 1H, *J* = 4.1, 6.8 and 13.2), 3.92-4.04 (m, 2H), 4.11-4.16 (m, 1H), 5.92 (t, 1H, *J* = 6.1), 6.86 (d, 2H, *J* = 8.0), 6.96 (t, 1H, *J* = 7.4), 7.24-7.29 (m, 2H), 7.69-7.74 (m, 2H), 7.81-7.86 (m, 1H), 8.12 (dd, 1H, *J* = 3.4 and 5.9). ν_{max} (Nujol) 3480 (OH), 3270 (NH), 1540 (NO_2), 1327 (SO_2N/NO_2), 1155 (SO_2N). *Anal. Calcd.* for $C_{15}H_{16}NO_6S$: C, 51.13; H, 4.58; N, 7.95. *Found*: C, 51.50; H, 4.79; N, 7.71.

General Method for the Preparation of 8a-c,e

In a round bottom flask (4-methylphenyl)sulfonyl chloride (5 mmol, 0.95 g) was dissolved in CH_2Cl_2 (5 ml) and pyridine (5 mmol, 0.40 g) was dropwise added at 0 °C. The solution was magnetically stirred at 0°C for 20 min and a solution of **7** (1 mmol) in 5 ml of CH_2Cl_2 added at the same temperature. After 20 min the temperature was raised to 40 °C and the solution stirred for the time indicated in Table 2. After cooling the crude was washed with 5% HCl, brine, dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The residue was purified by MPLC or flash column chromatography on silica gel (230-400 mesh). Starting amido alcohol, reaction time, chromatographic eluant, yield and physical, spectroscopic and analytical data of **8a-c,e** are as follows.

1-*N*-(4-Methylphenylsulfonyl)amino-2-*O*-(4-methylphenylsulfonyl)oxy-3-(phenoxy)propane (8a). **7a**; 5 h; Et_2O-PE 1:1. **8a**, 92%; mp 56-57 °C; ^1H NMR ($CDCl_3$), δ, 2.40 (s, 3H), 2.44 (s, 3H), 3.26-3.43 (m, 2H), 3.97 (dd, 1H, *J* = 5.0 and 10.7), 4.04 (dd, 1H, *J* = 5.2 and 10.7), 4.73-4.79 (m, 1H), 4.89 (t, 1H, *J* = 6.5), 6.64 (d, 2H, *J* = 8.1), 6.94 (t, 1H, *J* 7.3), 7.19-7.27 (m, 4H), 7.32 (d, 2H, *J* = 8.2), 7.68 (d, 2H, *J* = 8.2), 7.76 (d, 2H, *J* = 8.3). ν_{max} (Nujol) 3290 (NH), 1357 (SO_2O), 1336 (SO_2N), 1175 (SO_2O), 1158 (SO_2N). *Anal. Calcd.* for $C_{23}H_{25}NO_6S_2$: C, 58.09; H, 5.30; N, 2.95. *Found*: C, 58.50; H, 5.69; N, 2.81.

1-*N*-(4-Methylphenylsulfonyl)amino-2-*O*-(4-methylphenylsulfonyl)oxyoctane (8b). **7b**; 13 h; Et_2O-PE 1:1. **8b**, 84%; mp 79-80 °C; ^1H NMR ($CDCl_3$), δ, 0.75 (t, 3H, *J* = 6.9), 0.97-1.38 (m, 10H), 2.19 (s, 3H), 2.20 (s, 3H), 3.03-3.21 (m, 2H), 4.01 (m, 1H), 4.44 (t, 1H, *J* = 6.4), 7.32 (m, 4H), 7.71 (d, 2H, *J* = 8.3), 7.75 (d, 2H, *J* = 8.3). ν_{max} (Nujol) 3283 (NH), 1350 (SO_2O), 1325 (SO_2N), 1175 (SO_2O), 1153 (SO_2N). *Anal. Calcd.* for $C_{22}H_{31}NO_5S_2$: C, 58.25; H, 6.89; N, 3.09. *Found*: C, 58.60; H, 7.31; N, 2.89.

1-*N*-(4-Methylphenylsulfonyl)amino-2-*O*-(4-methylphenylsulfonyl)oxycyclohexane (8 c). **7c**; 24 h; Et_2O-PE 1:2. **8c**, 82%; mp 155-156 °C (lit.,[18] 149-151 °C); ^1H NMR ($CDCl_3$), δ, 1.16-1.25 (m, 4H), 1.32-1.40 (m, 1H), 1.55-1.63 (m, 1H), 1.74-1.82 (m, 1H), 2.15-2.22 (m, 1H), 2.41 (s, 3H), 2.45 (s, 3H), 3.09-3.18 (m, 1H), 4.18-4.25 (m, 1H), 4.90 (bs, 1H), 7.26 (d, 2H, *J* = 8.2), 7.33 (d, 2H, *J* = 8.2), 7.72 (d, 4H, *J* = 8.2).

1-*N*-(4-Methylphenylsulfonyl)amino-2-*O*-(4-methylphenylsulfonyl)oxy-3-(phenylmethoxy)propane (8e). **7e**; 24 h; Et_2O-PE 1:1. **8e**, 83%; oil; ^1H NMR ($CDCl_3$), δ, 2.42 (s, 6H), 3.15-3.29 (m, 2H), 3.43 (dd, 1H, *J* = 10.9 and 12.6), 3.51 (dd, 1H, J = 10.9 and 12.9), 4.37 (dd, 2H, *J* = 11.9 and 17.5), 4.58 (m, 1H), 4.75 (t, 1H, *J* = 6.5), 7.16-7.32 (m, 9H), 7.67 (d, 2H, *J* = 8.3), 7.73 (d, 2H, *J* = 8.3). ν_{max} (Nujol) 3235 (NH), 1340 (SO_2O), 1317 (SO_2N), 1181 (SO_2O), 1160 (SO_2N). *Anal. Calcd.* for $C_{24}H_{27}NO_6S_2$: C, 58.88; H, 5.56; N, 2.86. *Found*: C, 59.31, H, 5.82, N, 2.77.

1-*N*-(2-Nitrophenylsulfonyl)amino-2-*O*-(4-methylphenylsulfonyl)oxy-3-(phenoxy)propane (14). **13**; 3 h; Et_2O-PE 3:1. **14**, 86%; mp 107-108 °C; ^1H NMR ($CDCl_3$), δ, 2.41 (s, 3H), 3.48-3.63 (m, 2H), 4.06 (dd, 1H, *J* = 5.6 and 11.7), 4.14 (dd, 1H, *J* = 5.5 and 11.7), 4.82-4.90 (m, 1H), 5.71 (t, 1H, *J* = 6.9), 6.74 (d, 2H, *J* = 8.0), 6.98 (t, 1H, *J* = 7.3), 7.23-7.28 (m, 2H), 7.36 (d, 2H, *J* = 8.2), 7.70-7.74 (m, 2H), 7.81 (d, 2H, *J* = 8.3), 7.86-7.89 (m, 1H), 8.08-8.11 (m, 1H). ν_{max} (Nujol) 3336 (NH), 1543 (NO_2), 1346 (NO_2/SO_2O), 1340 (SO_2N), 1180 (SO_2O), 1175 (SO_2N). *Anal. Calcd.* for $C_{22}H_{22}NO_8S_2$: C, 52.16; H, 4.38; N, 5.53. *Found*: C, 52.70, H, 4.71, N, 5.21.

General Method for the Synthesis of Aziridines 9a-c,e.

The ditosylderivative **8** (1 mmol) was dissolved in acetonitrile and K_2CO_3 (4 mmol, 0.55 g) was added. After stirring at 45 °C for the indicated time (see Table 2) the crude was diluted with Et_2O or CH_2Cl_2 and water. The organic phase was washed with brine, dried (Na_2SO_4) and solvent was removed under reduced pressure, affording pure aziridines. Starting ditosyl, reaction time, yield and physical, spectroscopic and analytical data of aziridines **9a-c,e** are as follows.

***N*-(4-Methylphenylsulfonyl)-2-[(phenoxy)methyl]aziridine (9a).** **8a**; 40 min; 96%; mp 109-110 °C; ^1H NMR ($CDCl_3$), δ, 2.33 (d, 1H, *J* = 4.2), 2.44 (s, 3H), 2.78 (d, 1H, *J* = 7.1), 3.14 (m, 1H), 3.92 (dd, 1H, *J* = 6.0, 10.8), 4.04 (dd, 1H, *J* = 4.4, 10.8), 6.72 (d, 2H, *J* = 8.2), 6.92 (t, 1H, *J* = 7.4), 7.18-7.32 (m, 4H), 7.82 (d, 2H, *J* = 8.2). ν_{max} (Nujol) 1319 (SO_2N), 1159 (SO_2N). *Anal. Calcd.* for $C_{16}H_{17}NO_3S$: C, 63.34; H, 5.65; N, 4.62. *Found*: C, 63.51, H, 5.89, N, 4.90.

***N*-(4-Methylphenylsulfonyl)-2-*n*-hexylaziridine (9b).** **8b**; 60 min; 97%; mp 45-46 °C (lit.,[19] 45-47 °C); ^1H NMR ($CDCl_3$), δ, 0.84 (t, 3H, *J* = 6.6), 1.12-1.33 (m, 8H), 1.49-1.55 (m, 2H), 2.05 (d, 1H, *J* = 4.5), 2.43 (s, 3H), 2.63 (d, 1H, *J* = 7.0), 2.68 (m, 1H), 7.32 (d, 2H, *J* = 8.2), 7.81 (d, 2H, *J* = 8.2).

***N*-(4-Methylphenylsulfonyl)-7-azabicyclo[4.1.0]heptane (9c).** **8c**; 40 min; 96%; mp 54.5-55.5 °C (lit.,[20] 55.3-55.9 °C); ^1H NMR ($CDCl_3$), δ, 1.17-1.26 (m, 2H), 1.35-1.46 (m, 2H), 1.78-1.83 (m, 4H), 2.43 (s, 3H), 2.98 (m, 2H), 7.30 (d, 2H, *J* = 8.2), 7.81 (d, 2H, *J* = 8.2).

***N*-(4-Methylphenylsulfonyl)-2-[(phenylmethoxy)methyl]aziridine (9e).** **8e**; 40 min; 97%, mp 42 °C; ^1H NMR ($CDCl_3$), 2.21 (d, 1H, *J* = 4.5), 2.44 (s, 3H), 2.69 (d, 1H, *J* = 7.1), 3.01-3.08 (m, 1H), 3.45 (dd, 1H, *J* = 6.2 and 11.3), 3.63 (dd, 1H, *J* = 4.2 and 11.3), 4.45 (s, 2H), 7.20-7.36 (m, 7H), 7.85-7.89 (m, 2H). ν_{max} (Nujol) 1321 (SO_2N), 1160 (SO_2N). *Anal. Calcd.* for $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03; N, 4.41. *Found*: C, 64.80, H, 6.38, N, 4.62.

***N*-(4-Methylphenylsulfonyl)-2-phenylaziridine (9d).** Aziridine **9d** was prepared from **7d** under Mitsunobu conditions.[13] Diethyl azodicarboxylate (DEAD) (383 mg, 2.2 mmol) was added over 15 min to a THF (3 ml) solution of **7d** (583 mg, 2 mmol) and PPh_3 (551 mg, 2.1 mmol) maintained at 0 °C. The mixture was warmed to 20 °C over 16 h and evaporated. The residue was purified by flash chromatography (silica gel CH_2Cl_2:PE 1:2) affording 415 mg (76% yield) of the title compound. mp 87-88 °C (lit.,[20] 88-89 °C); ^1H NMR ($CDCl_3$), δ, 2.38 (d, 1H, *J* = 4.5), 2.43 (s, 3H), 2.97 (d, 1H, *J* = 7.2), 3.76 (dd, 1H, *J* = 4.5 and 7.2), 7.19-7.34 (m, 7H), 7.86 (d, 2H, *J* = 8.3).

***N*-(2-Nitrophenylsulfonyl)-2-[(phenoxy)methyl]aziridine (15).** Tosylate **14** (1 mmol, 507 mg) was dissolved in acetonitrile (0.5 ml) and lyophilised Na_2CO_3 (1 mmol, 106 mg) was added. After stirring at 80 °C for 1 h and the work-up described in the general method, the crude was purificated by flash column chromatography (AcOEt-PE 1:3) affording 274 mg (82% yield) of the title compound. ^1H NMR ($CDCl_3$), δ, 2.61 (d, 1H, *J* = 4.7), 3.02 (d, 1H, *J* = 7.1), 3.40-3.46 (m, 1H), 4.12 (dd, 1H, *J* = 4.4 and 11.0), 4.18 (dd, 1H, *J* = 5.0 and 11.0), 6.81 (d, 2H, *J* = 8.2), 6.94 (t, 1H, *J* = 7.3), 7.21-7.26 (m, 2H), 7.71-7.77 (m, 3H), 8.21 (m, 1H). ν_{max} (Nujol) 1543 (NO_2), 1337 (NO_2/SO_2N), 1168 (SO_2N). *Anal. Calcd.* for $C_{15}H_{14}N_2O_5S$: C, 53.88; H, 4.22; N, 8.38. *Found*: C, 54.11, H, 4.51, N, 7.95.

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